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(54) Selective solvent extraction
using organophosphorus and car-
boxylic acids

(57) A process for the extraction of
metal values, in particular divalent
metal ions such as copper, nickel,
zinc, cobalt and manganese from
aqueous solutions thereof which
may be well in the acid range for
example of pH 2 to 4. Extraction is
effected using known organophos-
phorus or carboxylic acid extrac-
tants but in combination with non-
chelating oximes, preferably of al-
dehydes wherein the alpha-carbon
atom is primary or secondary. A
synergistic effect between the ex-
tractant and oxime enables extrac-
tion to take place at a lower pH
than heretofore thereby saving in
acid and neutralizing agents in
many instances.

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Extraction, %

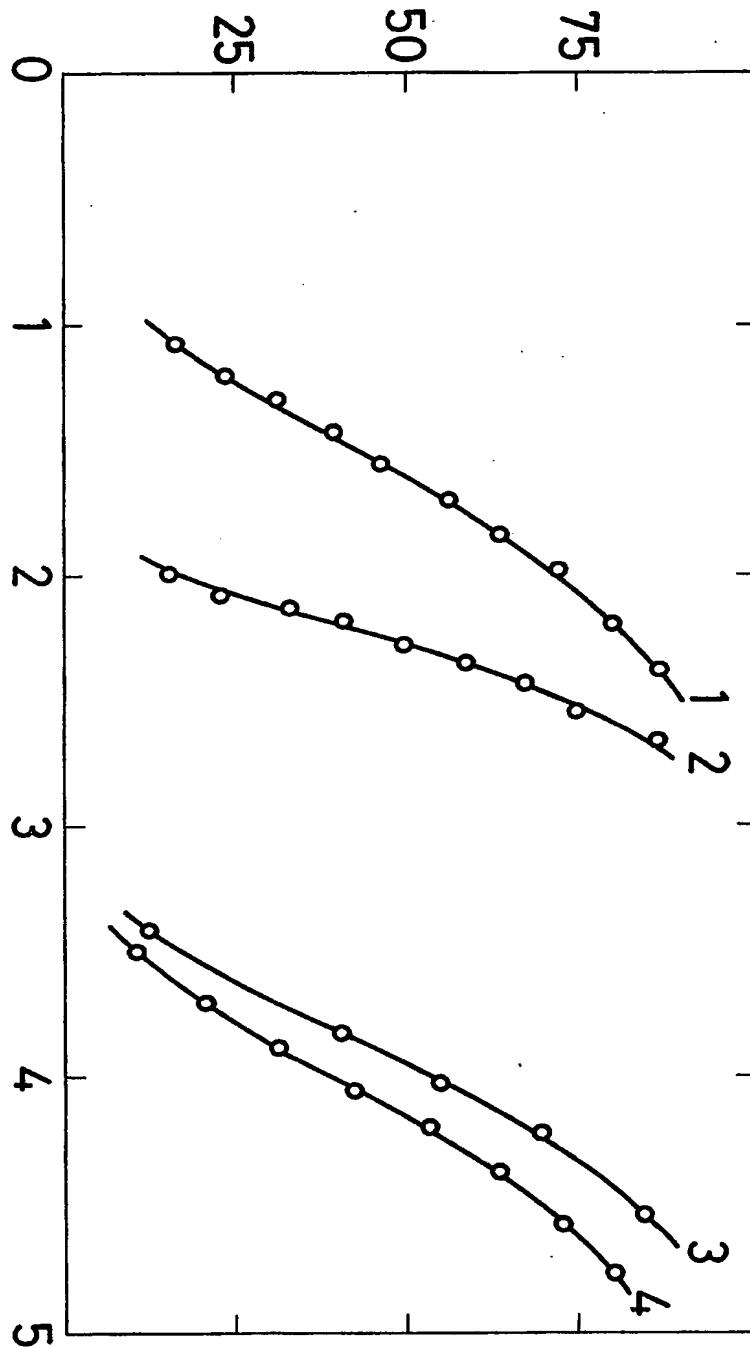


FIG. 1

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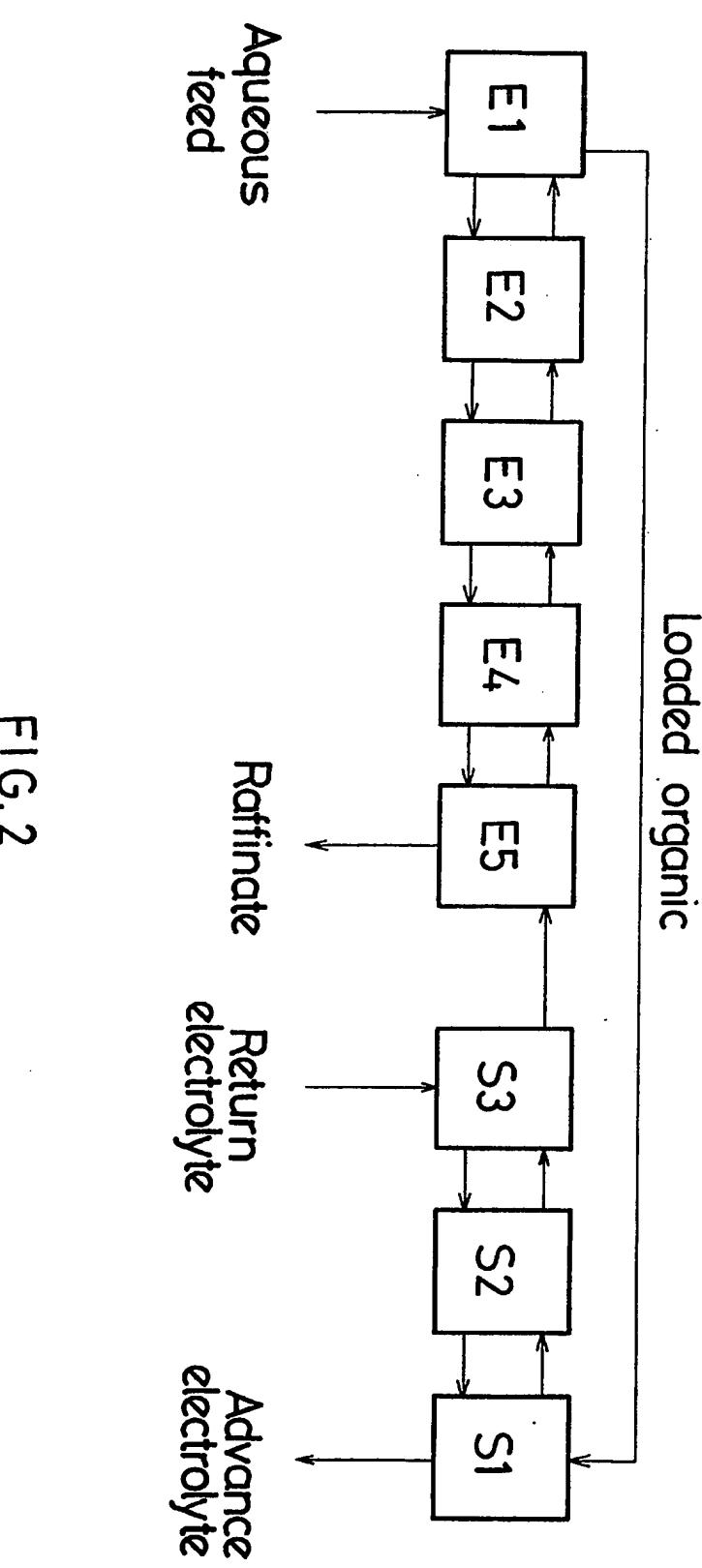


FIG. 2

SPECIFICATION**Selective solvent extraction using organophosphorus and carboxylic acids****5 BACKGROUND TO THE INVENTION**

5

THIS INVENTION relates to selective solvent extraction using organophosphorus and carboxylic acids as the metal extractants in the presence of additives which greatly enhance the utility of extractants under certain conditions.

It is often desirable to remove, and possibly recover, metals which are dissolved in a leaching step in hydrometallurgical processes. Metals which are often to be removed and recovered include cobalt, nickel, copper, zinc and manganese which are all amenable to removal by use of a solvent extractant.

10

However, as a result of the fact that leach liquors containing these metals usually result from a leach using acid, the pH of the leach liquor is generally rather low. Conventional solvent extractants such as organophosphorus and carboxylic acids only operate effectively at appreciably high pH and thus, either extremely poor performance must be tolerated, or the leach liquor must be at least partly neutralized thereby consuming both acid and alkali in order to achieve this. Once at least partially neutralized, the organophosphorus i.e. organophosphoric, organophosphonic and organophosphinic, and carboxylic acids operate effectively as solvent extractants. Usually, however, such a procedure is not favoured as it is uneconomical and it would be most desirable to provide a process for the extraction of such metals at a substantially lower pH than is at present possible.

15

It is known, and has been practiced, to employ di-(2-ethylhexyl) phosphoric acid at very mildly acidic pH. The phosphonic acid equivalent has also been employed with somewhat greater success and a phosphinic acid reagent has recently become available. The above-mentioned phosphoric acid has also been used together with chelating additives in the form of the commonly known hydroxyoxime sold under the Registered trade mark LIX63 by Henkel Corporation for separating copper and cobalt from nickel in sulphate streams. This process did not proceed, as far as Applicant is aware, beyond the pilot plant scale.

20

30 It is to be observed in connection with existing extraction processes, that cobalt is generally extracted at a lower pH value than is nickel.

30

BRIEF SUMMARY OF THE INVENTION

It has now surprisingly been found that an unforeseen extremely marked synergistic effect is obtained when there is used, together with an organophosphorus acid and any carboxylic acids having required extraction characteristics, a non-chelating oxime. This synergistic effect enables the metals to be extracted at substantially lower pH levels than was possible heretofore.

35

Accordingly this invention provides a process for the solvent extraction of metal values from solutions containing such metals comprising the contacting of a pregnant solution with a solvent extractant being an organophosphorus acid or a carboxylic acid capable of extracting desired metal values, the extraction being characterised by the fact that it takes place in the presence of a non-chelating oxime selected to enhance extraction of the desired metal values.

40

Further features of the invention provide for the oxime to be selected to enable extraction to take place at a lower pH than was practical heretofore; for the extractant to be organophosphoric acid of the type $(RO)_2 PO-OH$ where each R is, independently of the other, a substituted or unsubstituted alkyl, aryl, or alkaryl group; for the extracted metals to be cobalt, nickel, manganese, copper and zinc; for the extraction, in the case of organophosphoric acids to be carried out in the pH range of from 0 to 5, and in the case of carboxylic acids in the pH range of from 1 to 5, and for the contact time to be of the order of a few minutes.

45

50 The fact that a synergistic effect is created by employing non-chelating oximes together with the organophosphorus or carboxylic acids is evidenced by the fact that, in the case of cobalt and nickel, the order of extraction is entirely reversed so that the selectivity for cobalt over nickel is reversed. Also the extracted species are different: in the case of di-(2-ethylhexyl) phosphoric acid with 2-ethylhexanal oxime the cobalt is extracted as the bright pink octahedral complex as opposed to the dark blue tetrahedral complex whilst the nickel is extracted as the turquoise as opposed to the apple-green octahedral complex in which the oxygen-donor ligands have been replaced by nitrogen-donor ligands.

50

Not only does the present invention provide for extraction of metal values from solutions at a substantially lower pH than was heretofore possible, but the extraction takes place extremely quickly (of the order of a few minutes, as opposed to some hours in the case of a carboxylic acid and chelating oxime such as LIX 63 mixture) and, in addition, stripping of the extracted values from the solvent extractant has proved to be extremely simple. One reason for this is the avoidance of the formation of intractable cobalt (III) chelate complexes which are not amenable to conventional stripping techniques. Thus, stripping can be effected simply by using dilute mineral acid solutions for example 20 to 200 g/l sulphuric acid.

55

65

Also, some mixtures, for example 2-bromo octanoic acid mixed with 2-ethylhexanal oxime show useful separations of nickel which is extracted at pH 2 to 3 from cobalt which is extracted at pH 3 to 4 as opposed to the non-selective extraction of both metals together at a pH of 4 to 5 in the case of the carboxylic acid alone.

5 Preferably, the oximes employed in the implementation of the invention are those of aldehydes having the alpha-carbon as a primary or secondary one. Other oximes show similar synergistic effects. 5

It will be understood that the organophosphorus acids which can be used to extract cobalt, nickel, manganese and copper in the pH range from 0 to 2 enables these metals to be

10 recovered directly from acid leach liquors without the necessity of partially or totally neutralizing 10 the residual acid concentration of the leach liquors. This represents a substantial saving of both acid and neutralizing agents.

BRIEF DESCRIPTION OF THE DRAWINGS

15 Figure 1 is a series of graphs showing percentage extraction vs pH for four different extractant 15 systems and,

Figure 2 is a schematic flow sheet of a continuous counter current extraction process.

DETAILED DESCRIPTION OF VARIOUS EMBODIMENTS OF THE INVENTION

20 Initial Tests

In order to investigate and confirm the operation of the invention initial tests were carried out under fixed conditions in order to determine the pH at which 50 per cent extraction would take place (pH 0,5) in the case of nickel and cobalt. These results are given in the Table below with each result having been obtained by investigating the extraction of cobalt and nickel by 0,5M

25 organophosphorus acid in xylene at 20°C. In each case where an additive was added the extent of addition was also 0,50M. In each case the aqueous solutions contained 0,10M cobalt (II) and/or 0,10M nickel as the nitrate in 1,00M ammonium nitrate solution. The organophosphoric, organophosphonic and organophosphinic acids were investigated, the latter two being commercially available reagents RD 577 marketed by Shell Chemicals and Cyanex CNX

30 marketed by the American Cyanamid Company in the case of the phosphonic and phosphinic acid reagents respectively. 30

35	Extractant	Additive†	pH _{0,5}		ΔpH _{0,5} ††		35
			Co	Ni	Ni - Co	Co	
40	Di-(2-ethyl-hexyl) Phosphoric Acid (D2EHPA)	None	3,68	4,11	0,43	0,00	0,00
		TBP	3,82	4,07	0,25	-0,14	0,04
		isodecanol	3,65	3,86	0,21	0,03	0,25
		nonylphenol	3,70	3,91	0,21	-0,02	0,20
		TOPO	3,90	4,10	0,20	-0,22	0,01
		LIX 63	0,12	ND*	ND	3,56	ND
45	RD577	EHO	1,99	1,58	-0,41	1,69	2,53
		None	3,90	5,12	1,22	0,00	0,00
		TBP	3,99	4,98	0,99	-0,09	0,14
		isodecanol	4,12	4,77	0,65	-0,22	0,35
		EHO	3,25	3,06	-0,19	0,65	2,06
		CNX	None**	4,22	5,20	0,98	0,00
50		EHO**	4,22	4,58	0,36	0,00	0,62
							50
55							55

†TBP = Tri-n-butyl phosphate; TOPO = tri-n-octylphosphine oxide; EHO = 2-ethylhexanal oxime

††ΔpH_{0,5} = pH_{0,5}^{without additive} - pH_{0,5}^{with additive}

*not determined due to extremely slow extraction rate of nickel

60 **solutions include 25 volume % isodecanol 60

It will be noted that only small influences on the pH_{0,5} were obtained in all cases apart from those in which 2-ethylhexanal oxime and LIX63 were employed. Whilst a vast improvement was obtained in the case of LIX63 with the organophosphoric acid in respect of cobalt, the extraction 65 of nickel was too slow to be of any practical use and thus, at the best, this additive could be 65

employed for separating cobalt from nickel. However, it must be borne in mind that extraction of cobalt even is slow and also stripping thereof from the reagent is extremely difficult.

In all other cases nickel pH recovery is substantially improved and an examination of the pH figures given in the cobalt and nickel columns shows that the oxime additive has by far the most 5 desirable effect at lowering the pH value at which extraction takes place. This is, of course, with the exception of LIX63 the disadvantages of which are discussed above. 5

The pH extraction curves were plotted for various systems and exemplary curves are illustrated in Fig. 1. In Fig. 1, the curve numbered 1 is that of the synergistic mixture of 0.5M Di-(2-ethylhexyl) phosphoric acid and 0.5M 2-ethylhexanal oxime.

10 Curve numbered 2 is that of 0.5M RD573 (a commercially available chelating di-oxime made by Shell Chemicals) and only approaches the performance of the synergistic mixture of the invention. This chelating di-oxime has the disadvantage indicated above in that intractible cobalt complexes will arise unless a high selectivity over cobalt is exhibited.

Curve numbered 3 is that of 0.5M LIX65N (a variant of LIX63 and also made by Henkel 15 Corporation).

Curve numbered 4 is that of 0.5M Di-(2-ethylhexyl) phosphoric acid itself.

The curves were obtained using an aqueous phase of 0.1M Ni (NO₃)₂ in 1.0M NH₄NO₃ and the organic solvent was xylene. The temperature was 20°C, aqueous to organic ratio 1:1 and the contact time 10 minutes except in the use of LIX65N where the contact time was 60 20 minutes. 20

The superiority of the synergistic mixture of the invention is quite obvious from the curves which show that extraction takes place over the range of about pH 1 to pH 2, for the mixture.

Different Oximes

25 Tests were conducted to show that different oximes of the non-chelating type exhibited the same synergistic effect. In these tests the pH_{0.5} was again determined from the same 0.1M nitrate solutions employed in the previous tests. The aqueous to organic ratio was 1:1 and the organic phase was a 0.5M solution of oxime plus 0.5M Di-(2-ethylhexyl) phosphoric acid. The temperature was 20°C. 25

30 The oximes employed were all of the non-chelating type having the general formula R.CNOH.R' in which R and R' had the meanings set out in the following Table 2:- 30

TABLE 2
Extraction of nickel and cobalt by mixtures of Di-(2-ethylhexyl) phosphoric acid and 35 non-chelating oximes, R.CNOH.R'. 35

R	R'	pH _{0.5}			ΔpH _{0.5}		40
		Ni	Co	Co-Ni	Ni	Co	
C ₇ H ₁₅	H	1.34	1.72	0.38	2.77	1.96	
C ₄ H ₉ CH(C ₂ H ₅)	H	1.58	1.99	0.41	2.53	1.69	
C ₂ H ₅ CH(C ₂ H ₅)	H	1.73	2.13	0.40	2.38	1.55	
C ₆ H ₅	H	3.41	3.25	-0.16	0.70	0.43	
(CH ₃) ₃ C	H	3.46	3.50	0.04	0.65	0.18	45
C ₆ H ₁₃	CH ₃	3.80	3.49	-0.31	0.31	0.19	
C ₅ H ₁₁	C ₂ H ₅	3.94	3.59	-0.35	0.17	0.09	
C ₆ H ₅	CH ₃	4.03	3.71	-0.32	0.08	-0.03	
(CH ₃) ₂ CH	(CH ₃) ₂ CH	4.15	3.77	-0.38	-0.04	-0.09	50

Useful synergistic effects (i.e., large ΔpH_{0.5} values) are shown for the oximes of aldehydes where the alphacarbon is primary or secondary. Other oximes (namely those of aldehydes where the alpha-carbon is tertiary, aromatic aldehydes, and aliphatic or aromatic ketones) show very much 55 smaller synergistic effects. Note that a positive value in the column headed pH_{0.5} (Co-Ni) indicates that the mixture is selective for nickel over cobalt, whilst a negative value indicates selectivity for cobalt over nickel. 55

Different Organophosphoric Acids

60 Tests were conducted under the same conditions as for the preceding set of tests but with different organophosphoric acids and 2-ethylhexanal oxime as the non-chelating oxime. The different acids used were those having the following formulae:- 60

5		5
	Acid No. (Ia)	
10		10
	Acid No. (Ib)	
15		15
20		20
	Acid No. (Ic)	
25		25
	Acid No. (Id)	
30		30
35		35
	Acid No. (Ie)	
40		40
45		45
	Acid No. (If)	
50		50
	The results are set forth in the following Table 3:-	

TABLE 3

Extraction of nickel and cobalt by mixtures of organophosphoric acids and 2-ethylhexanal oxime.

Organophosphoric Acid	pH _{0.5} for acid alone			pH _{0.5} for acid plus oxime			$\Delta pH_{0.5}$	
	Ni	Co	Ni-Co	Ni	Co	Co-Ni	Ni	Co
Ia	4.11	3.68	0.43	1.58	1.99	0.41	2.53	1.69
Ib	3.72	3.42	0.30	1.30	1.70	0.40	2.42	1.72
Ic	2.92	2.85	0.07	0.84	1.23	0.39	2.08	1.62
Id	2.71	2.50	0.21	0.66	0.98	0.32	2.05	1.52
Ie	2.30	2.30	0.00	0.81	1.18	0.37	1.49	1.12
If	2.63	2.53	0.10	0.42	0.79	0.37	2.21	1.74

$$\Delta pH_{0.5} = pH_{0.5} \text{ for acid alone} - pH_{0.5} \text{ for acid plus oxime.}$$

These results show that by varying the molecular structure of the organophosphoric acid, in particular by introducing aromatic functions, extraction of cobalt and nickel can be carried out under remarkably acidic conditions and that extractant mixtures can be formulated for the relevant circumstances.

It is to be noted that the selectivity of the organophosphoric acids for cobalt over nickel (column 4) becomes one of nickel over cobalt for the mixed extractants (column 7).

Different Carboxylic Acids

Tests were conducted on carboxylic acids with 0.5M carboxylic acid (1.0M for Versatic 10) plus, where applicable, 0.5M non-chelating oxime in xylene (one result labelled† used heptane as the diluent). The aqueous phase contained 0.1M Ni(NO₃)₂ or 0.1M Co(NO₃)₂ in 1.0N NH₄NO₃. Contact was made at aqueous to organic ratio of 1:1.

The results obtained are reflected below:—

Extraction of nickel and cobalt by mixtures of carboxylic acids and non-chelating oximes.

Carboxylic acid	Non-chelating oxime†	pH _{0.5}			$\Delta pH_{0.5}$	
		Ni	Co	Co-Ni	Ni	Co
Versatic 10	None	5.98	6.16	0.18	0.00	0.00
Versatic 10	CAO	4.22	5.01	0.79	1.76	1.15
Versatic 10	EHO	4.66	5.28	0.62	1.32	0.88
2-bromolauric	None	4.68	4.70	0.02	0.00	0.00
	EHO	2.56	3.47	0.91	2.12	1.23
2-bromocaprylic	CAO	2.34	3.30	0.96	ND	ND
	EHO	2.42	3.61	1.19	ND	ND
50	EHO‡	1.96	3.20	1.24	ND	ND
	EBO	2.70	3.70	1.00	ND	ND

†CAO, caprylaldehyde oxime; EHO, 2-ethylhexanal oxime; and EBO, 2-ethylbutanal oxime.

Versatic 10 is a highly branched carboxylic acid produced by Shell Chemicals. Although mixtures of carboxylic acids and non-chelating oximes do not permit extraction of cobalt and nickel under as acidic a condition as mixtures of organophosphoric acids and non-chelating oximes, the nickel-over-cobalt selectivity of the former mixtures (column 5) are significantly higher than the latter (column 7 in Table 2) and the required pH is certainly lower.

Effects on Different Cations

Tests were carried out on numerous different cations, generally metal ions, in order to ascertain the effect of the non-chelating oxime. The tests were conducted, as before, by determining the pH_{0.5} in each case. All cations were present as nitrates in 1M HNO₃ and the pH

was adjusted using concentrated ammonia solution. The exceptions to the above were the ferrous Fe^{2+} ion which was in the sulphate form in HNO_3 initially and the Cr^{2+} and VO^{2+} cations which were in the sulphate form in 0,33M H_2SO_4 , the pH of which was adjusted using NaOH.

5 The extractant was 0,5M Di-(2-ethylhexyl) phosphoric acid (D2EHPA) and 0,5 M2EHPA in admixture with 0,5M 2-ethylhexanal oxime in xylene in each case and at 20°C. Contact took place at an aqueous to organic ratio of 1:1. 5

The results of the tests are reflected in Table 5 below:-

10	Metal	$\text{pH}_{0.5}(\text{D2EHPA})$	$\text{pH}_{0.5}(\text{D2EHPA-EHO})$	$\Delta\text{pH}_{0.5}\ddagger$	10
15	Ni^{2+}	4,12	1,60	2,52	
	Cu^{2+}	2,90	1,05	1,85	
	Co^{2+}	3,70	2,00	1,70	15
	Fe^{2+}	3,56	2,10	1,46	
	Mn^{2+}	2,90	2,12	0,78	
	Cr^{2+}	2,15	1,47	0,68	
	VO^{2+}	1,25	0,96	0,29	
20	Fe^{3+}	-0,32	-0,40	0,08	20
	Cr^{3+}	3,12	2,98	0,14	
	La^{3+}	1,96	2,06	-0,10	
25	Mg^{2+}	3,81	3,69	0,12	25
	Ca^{2+}	2,85	2,97	-0,12	
	Zn^{2+}	1,42	1,58	-0,16	
	Cd^{2+}	2,98	1,48	1,50	
	Ag^+	3,25	< 0,00	> 3,25	
30	Pb^{2+}	2,50	2,33	0,17	30
	NH_4^+	3,57*	3,37*	0,20	

$$\ddagger \Delta\text{pH}_{0.5} = \text{pH}_{0.5}(\text{D2EHPA}) - \text{pH}_{0.5}(\text{D2EHPA-EHO})$$

*pH at which the NH_4^+ concentration in the organic phase

35 reaches 0,05M. 35

Appreciable synergistic effects are shown by all the diivalent transition metal ions studied (note that VO^{2+} , however, has only one "vacant" coordination site once complexed with D2EHPA, in contrast to two for the other divalent metal ions). There is no synergistic effect for trivalent ions.

40 Amongst the non-transition metals, only silver and cadmium show significant synergistic effects. 40
The implications for extraction of the divalent transition metals without co-extraction of gangue metals (magnesium, calcium, etc) or neutralization products (e.g. ammonium ion) are clear.

Continuous Counter-Current Extraction

45 Based on information collected a counter current type of extraction process was tested using a Bell-Engineering mixer-settler apparatus. The test extraction was that of nickel as it showed excellent sensitivity to the non-chelating oxime synergistic effect. The test work which will not be described in detail herein resulted in good extractions of Ni taking place over five extraction stages E1 through E5 as shown in Fig. 2. Three stripping stages are employed. 45

50 Typical operating conditions were found to be as indicated below in the case of use with and without the oxime. The system tested had organic phases consisting of 15% D2EHPA and 15% D2EHPA together with 5% EHO in Solvesso 150 as solvent. (Solvesso is an aromatic type of solvent sold under Trade Mark "Solvesso 150" by Esso Chemicals.

The organic to aqueous ration was 2,6:1 to give the conditions described below and a 50
55 residence time of 2,75 minutes was allowed in each mixer. The conditions were then as shown in Table 6:- 55

TABLE 6

System	Extraction pH	Nickel in raffinate g l ⁻¹	NH ₃ in loaded organic phase g l ⁻¹	
15% D2EHPA	4,4-4,5	0,04	1,09	5
15% D2EHPA 5%	2,8-3,2	0,02	0,024	
EHO				10

A comparison of the acid-base requirements for the D2EHPA and D2EHPA-EHO systems given below in Table 7:-

15 TABLE 7

	D2EHPA (%)	D2EHPA-EHO(%)	
Ammonia for pH adjustment during extraction	125-133	85-98	20
Acid make-up for return electrolyte	25-33	16‡	
Sodium hydroxide for pH adjustment of advance electrolyte	<1	5‡	25
Total acid-base requirement	150-167	106-119	

30 The improvement as a result of the invention is thus, to say the least, appreciable. The invention therefore provides a simple yet effective process for the extraction of metal values by means of organophosphorus and carboxylic acids in combination with non-chelating oximes.

35 CLAIMS

1. A process for the solvent extraction of metal values from solutions containing such metals comprising the contacting of a pregnant solution with a solvent extractant being an organophosphorus acid or a carboxylic acid capable of extracting desired metal values, the extraction being characterised by the fact that it takes place in the presence of a non-chelating oxime selected to enhance extraction of the desired metal values.
2. A process as claimed in claim 1 in which the non-chelating oxime is selected to enable extraction to take place at a lower pH than was previously practiced.
3. A process as claimed in either of the preceding claims in which the solvent extractant is an organophosphorus acid of the general formula (RO)₂PO-OH where each R is, independently of the other, a substituted or unsubstituted alkyl, aryl or alkaryl group.
4. A process as claimed in any one of the preceding claims in which the non-chelating oxime is one of an aldehyde where the alpha-carbon is primary or secondary.
5. A process as claimed in any one of the preceding claims 1 to 3 and in which the non-chelating oxime is one of those specifically herein identified.
6. A process as claimed in any one of the preceding claims in which the organophosphorus or carboxylic acid is any one of those specifically identified.
7. A process as claimed in any one of the preceding claims in which the process is one for the extraction of nickel, cobalt, manganese or copper.
8. A process as claimed in any one of the preceding claims in which the extraction is carried out at a pH of less than 5.
9. A process as claimed in claim 8 in which the extraction is carried out at a pH of less than 4.
10. A process substantially as herein described or exemplified.
11. Metals wherever separated by a method embodying the process of any one of claims 1 to 10.

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